Analysis of a Cocurrent Membrane Reactor

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Introduction

The use of membranes for gas separation continues to be of immense interest for industrial applications. In recent years their use in reactor engineering for selective separation of gaseous products resulting in favorable chemical equilibrium shift has been recognized. (Shah et al., 1970; Hwang and Kammermeyer, 1975). The use of microporous membranes to increase the conversion of reversible reactions by separating the gaseous product consisting of light molecules such as hydrogen has been studied by a number of researchers (Ito et al., 1984, 1985; Kameyama et al., 1981).

In this paper dehydrogenation of cyclohexane on a Pd-Al_2O_3 or Pt-Al_2O_3 has been studied in a permeable wall membrane reactor (perm-reactor). It is assumed that the catalyst is only present inside the tube with no reaction occurring on the shell side. A schematic diagram of the membrane reactor is shown in Figure 1.

Model Development

The dehydrogenation of cyclohexane reaction is of the form

$$aA = bB + cC \tag{1}$$

where $a = 1, b = 1, c = 3, A = C_6H_{12}, B = C_6H_6, C = H_2$.

The various parameters used in this study are tabulated in Table 1; the dimensionless equations governing the perm-reactor are summarized in Table 2.

The model uses several assumptions:

1. Isothermal operation
2. Negligible pressure drop on tube and shell sides
3. Plug flow on both tube and shell sides
4. No axial or radial diffusion.

Isothermal operation is valid since the conversion is low (7%) with no inerts and increases only with inert flow rate. Diffusion on shell side and tube side is neglected since the Peclet number is small. Plug flow is assumed on the tube side since the Reynolds number is large.

The model equations are solved as an initial value problem using Hammings' fourth-order predictor-corrector method. The feed is assumed to be product-free and only inert enters the shell side.

Results and Discussion

The conversion in the perm-reactor is defined as

$$X = 1 - (F_A^* + Q_A^*) \tag{2}$$

The main parameters that have been identified in our study are conversion, X; rate of permeation/rate of reaction, h; dimensionless reactor length, Z; equilibrium constant, K_P; pressure ratio, P_r; dimensionless inert flow rates on tube and shell sides, C_t and C_s; and permselectivity of cyclohexane and benzene with respect to hydrogen, u_A and u_B.

In Figure 2 the conversion obtained in the perm-reactor has been plotted as a function of the parameter h. The dimensionless reactor length Z is varied at pressure ratios of 0.0 and 1.0. Note that for low values of Z the conversion initially increases, then decreases. The increase is due to equilibrium shift resulting from permeation of product; the decrease is due to the loss of reactant at higher values of h. For a pressure ratio of 0.0, no maximum is observed at high values of Z since there is not enough reactant on the tube side. For a pressure ratio of 1.0, at high Z's the conversion levels off with increasing h as there is backpermeation of reactant and product from shell side to tube side, causing the reaction to remain in the forward direction but to proceed very slowly.

In Figure 3 the volume ratio, V_R, has been plotted vs. the optimum conversion ratio for various pressure ratios. The volume ratio is defined as the tube volume of the perm-reactor for optimum conversion divided by the volume of a tubular reactor for equilibrium conversion. Optimum conversion in the perm-reactor is attained when the reaction rate, f_A, goes to zero. The conversion ratio, X_R, is defined as the optimum conversion in a perm-reactor divided by the equilibrium conversion in a tubular reactor.

Note that for a pressure ratio of 0.0, the optimum conversion ratio is the highest and decreases with increasing pressure ratio.

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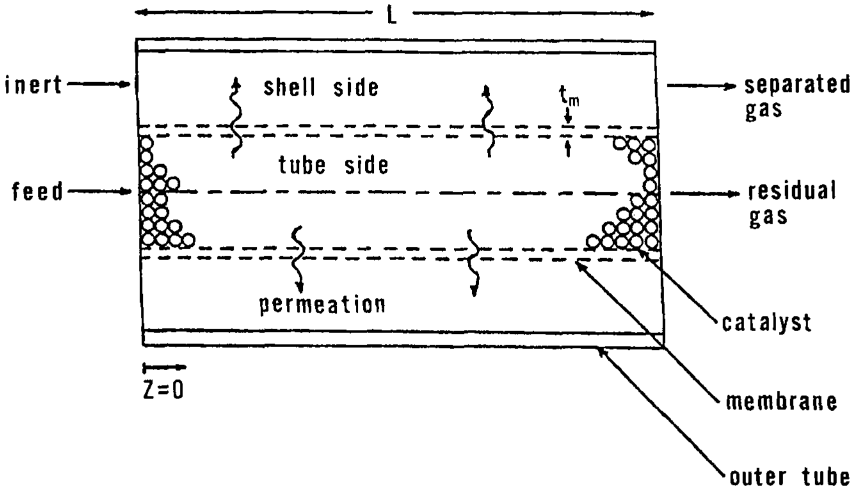

Figure 1. Diagram of perm-reactor.

This is for the most part attributed to equilibrium shift occurring due to permeation of product. At higher pressure ratios the amount of equilibrium shift decreases. As seen in Figure 3, for high values of h the optimum conversion ratio decreases due to increasing reactant loss from tube side to shell side at low pressure ratios, and due to back-permeation of hydrogen from shell side to tube side at high pressure ratios.

Table 1. Parameters Used in Study*

Reaction temperature, $T = 477$K

Reaction pressure, $P_t = 101.3$ kPa

Reaction rate constant, $k = 1.42 \times 10^{-5}$ mol/m$^3 \cdot$ s $\cdot$ Pa

Equilibrium constant, $K_P = 4.36 \times 10^{11}$ Pa^3

Permselectivities, $u_A = 0.274$
$u_B = 0.451$
$u_I = 0.224$

*Data from Ito et al. (1985).

Table 2. Model Equations

For the tube side, $Z > 0$

$$dF_A^*/dZ = -af_A - hu_A(x_A - y_AP_r) \tag{3}$$

$$dF_B^*/dZ = bf_A - hu_B(x_B - y_BP_r) \tag{4}$$

$$dF_C^*/dZ = cf_A - h(x_C - y_CP_r) \tag{5}$$

$$dF_I^*/dZ = -hu_I(x_I - y_IP_r) \tag{6}$$

For the shell side, $Z > 0$

$$dQ_A^*/dZ = hu_A(x_A - y_AP_r) \tag{7}$$

$$dQ_B^*/dZ = hu_B(x_B - y_BP_r) \tag{8}$$

$$dQ_C^*/dZ = h(x_C - y_CP_r) \tag{9}$$

$$dQ_I^*/dZ = hu_I(x_I - y_IP_r) \tag{10}$$

The effect at a pressure ratio of 1.0 has not been indicated in Figure 3, as the optimum conversion ratio is independent of h. There is back-permeation of both reactant and products and there is no appreciable loss of cyclohexane due to permeation. The extent of equilibrium shift is less than that at a lower pressure ratio due to greater back-permeation of products.

In Figure 4 the optimum conversion ratio for a fixed h is plotted vs. the permselectivity of cyclohexane with respect to hydrogen, for different permselectivities of benzene. Note that as the reactant permselectivity increases, the conversion ratio decreases due to increasing loss of reactant. For higher permselectivities of benzene, the conversion ratio increases due to increasing equilibrium shift.

When the pressure ratio is increased from 0.5 to 1.0, the conversion ratio for a fixed permselectivity of benzene approaches a limiting value with increase in the permselectivity of cyclohexane. As explained earlier this is due to the back-permeation of

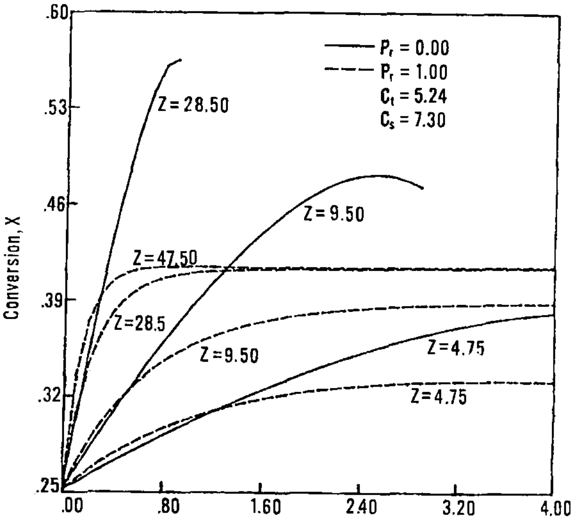

Figure 2. Effect of permeation rate/reaction rate ratio on perm-reactor conversion.

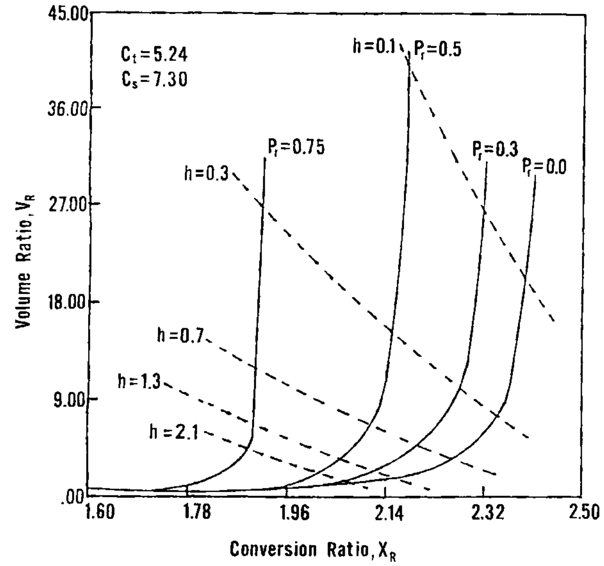

Figure 3. Volume ratio vs. optimum conversion ratio for various ratios of permeation rate to reaction rate at different pressure ratios.

reactant from shell side to tube side. The behavior is similar to that depicted in Figure 2.

The effect of inert flow rates has been shown in Figure 5. For a fixed pressure ratio, the conversion ratio has been plotted vs. the ratio of inert flow rate on the tube and the reactant flow rate at the inlet (C_t). The parameter is the ratio of inert flow on the shell side and the reactant flow rate at the inlet (C_s). The basic effect of inerts is to reduce the partial pressure of gases on both the shell and tube sides. Hence the greater the partial pressure difference the greater the equilibrium shift. Thus with increase in inert flow rate on the tube side there is a decrease in the conversion ratio.

For the hypothetical situation when there is no inert flow on the shell side and the pressure ratio is maintained at 1.0, there is hardly any equilibrium shift. The forward reaction quickly goes to zero as there is a buildup of products on the tube side. The initial rise of conversion ratio is due to the decrease in the permeation of cyclohexane at the inlet of the perm-reactor.

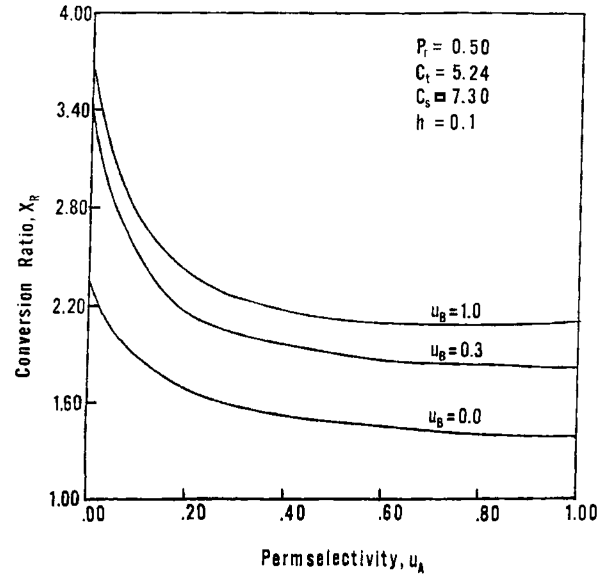

Figure 4. Effect of permselectivity of reactant and products on conversion.

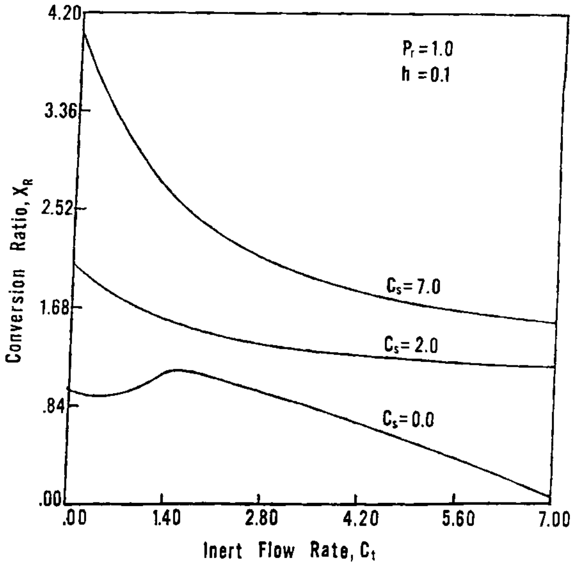

Figure 5. Effect of inert flow rates on conversion.

Summary

The following conclusions can be drawn from this study:

1. For a fixed length of perm-reactor there exists an optimum ratio of permeation rate to reaction rate h corresponding to the maximum conversion in Figure 2.

2. There exists a maximum (optimum) conversion in a cocurrent perm-reactor that is achieved when the forward reaction rate becomes zero.

3. When there is no back-permeation of reactant from the product (shell) side to the reactant (tube) side the optimum conversion in the perm-reactor is a function of the amount of permeation of cyclohexane. Thus the smaller the pressure ratio (P_r) and h, the larger the conversion.

For fixed inert flow rates on the reactant and product sides, and fixed pressure ratio P_r, there exists a conversion which is the maximum that can be attained in a reactor of reasonable length. This is evident from Figure 3.

4. When there is back-permeation of reactant from shell side to tube side, the optimum conversion in the perm-reactor is independent of h. For a perm-reactor operating in this regime there is a limiting length Z beyond which there is no appreciable change in conversion.

5. A membrane that exhibits a high permselectivity for the products over the reactants should be used in order to achieve large values of conversion.

6. There exists a critical value of inert flow rate on the shell side for a given inert flow rate on the tube side, which corresponds to the optimum conversion ratio of 1.0.

Acknowledgment

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Notation

A_m = area of membrane per unit length of perm-reactor, m^2/m
C_s = dimensionless flow of inert at inlet on the shell side, Q_{IO}/F_{AO}
C_t = dimensionless flow of inert at inlet on tube side, F_{IO}/F_{AO}
f_A = dimensionless rate expression for reaction $x_A^a - x_B^b x_C^c P_t^{(b+c-a)}/K_P$
F_i = molar gas flow rate in the tube side, mol/s
F_i^* = dimensionless flow of gas on the tube side, F_i/F_{AO}
h = ratio of permeation rate to reaction rate, $P^e A_m P_t / k v_t P_t^a t_m$
k = reaction rate constant, $mol/m^3 \cdot s \cdot Pa$
K_P = equilibrium constant, Pa^3
L = length of reactor, m
P^e = permeability of fast gas, $mol/m \cdot Pa \cdot s$
P_t = tube-side pressure, Pa
P_s = shell-side pressure, Pa
P_r = P_s/P_t
Q_i = molar gas flow rate on the shell side, mol/s
Q_i^* = dimensionless flow of gas on the shell side, Q_i/Q_{AO}
t_m = thickness of membrane, m
T = reaction temperature, K
u_i = permselectivity of gas i with respect to the fastest gas
v_t = tube side volume per unit length of perm-reactor, m^3/m
V_R = volume ratio, tube side volume of perm-reactor/volume of impermeable wall plug-flow reactor
x_i = mole fraction of gas in the tube side
X = conversion
X_R = conversion ratio, perm-reactor conversion/equilibrium conversion
y_i = mole fraction of gas on the shell side
Z = dimensionless perm-reactor length, $kP_t L V_t / F_{AO}$, Damkohler number

Subscripts

A = cyclohexane
B = benzene
C = hydrogen
I = inert
i = A, B, C, or I
O = perm-reactor inlet

Superscript

* = indication of being dimensionless

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